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PATENT SPECIFICATION

602,263

Application Date: July 6, 1945. No. 17353/45.

Complete Specification Accepted: May 24, 1948.

Index at acceptance:—Classes 1(i), F3a1a; and 2(iii), B1.

COMPLETE SPECIFICATION

Improved Process for the Dehydrogenation of Butenes

(A communication from STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America).

I, JOHN CONRAD ARNOLD, a British subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the catalytic dehydrogenation of butenes to butadiene using a finely divided fluidised dehydrogenation catalyst.

In prior processes, it has been difficult to carry out dehydrogenation operations in which high concentrations of catalyst and short contact or reaction times are used.

In the catalytic dehydrogenation of butenes to produce butadiene, it is necessary to expose butene at reaction temperature to a relatively large amount of catalyst and at the same time limit the time of contact of the butene with the catalyst at reaction temperature to a minimum to minimize side reactions or thermal cracking.

In my foreign correspondents' earlier Specification No. 557,624 there is described a process for the dehydrogenation of butene to butadienes in which a mixture of butenes and fluidised dehydrogenation catalyst passes overhead from a reactor to a gas-solids separating device, in which the gaseous reaction products are separated from the catalyst and recovered, the reaction products being quenched with a quenching fluid before or after separation from the catalyst and a part of the separated catalyst being passed to a regenerator in which it is regenerated in the presence of free oxygen e.g. air, and recycled to the reactor, and a part of the

separated catalyst being recycled directly to the reactor without regeneration.

The present invention comprises a process for the catalytic dehydrogenation of butenes to produce butadiene comprising introducing a gaseous fluid reactant containing butene, steam and a hydrocarbon dehydrogenation catalyst, not deactivated by steam, in powder form, into the lower portion of a reaction zone, passing the gaseous fluids upwardly through said reaction zone at a velocity sufficient to suspend the catalyst particles in the rising gases and forming a dry dense liquid-like catalyst-gas mixture, maintaining said reaction zone completely full of this fluidized catalyst-gas mixture, removing gaseous reaction products overhead with the catalyst in said catalyst-gas mixture, separating the bulk of the catalyst particles from the removed reaction products, quenching the separated reaction products to a temperature of 500–1000° F. to minimize losses of butadiene, returning a controlled amount of the separated catalyst particles as a confined stream to said reaction zone without regeneration to aid in maintaining the high concentration of catalyst in said reaction zone, suspending a second portion of said separated catalyst in a stream of steam superheated to a temperature above 1200° F., passing this suspension through a regeneration zone and returning the hot regenerated catalyst to said reaction zone.

In the accompanying drawing, the Figure represents one form of apparatus which may be used to carry out the invention.

Referring now to the drawing; the reference character (10) designates a cylindrical reaction zone or vessel provided at its bottom portion with an inlet (12) for feeding the gaseous reactant to the reactor. The reaction vessel (10) is provided in its lower portion with a perforated distribution member or grid member (14) for distributing the gaseous feed across the area of the reaction zone or

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vessel (10). Hot regenerated catalyst is introduced into the reactor (10) through standpipe (16) provided with one or more fluidizing lines (18) for maintaining the hot regenerated catalyst in fluidized condition in the standpipe (16).

The lower portion of the standpipe (16) is preferably provided with a control valve or damper (22) for regulating the amount of hot regenerated catalyst particles introduced into the reaction zone or vessel (10). Valve (22) may be controlled by mechanism responsive to the temperature in the reactor (10) or the regenerator later to be described. The standpipe (16) opens into the lower portion of the reaction zone (10) above the distribution member (14). The gaseous reactant passing upwardly through the reaction vessel (10) maintains the catalyst or contact particles in a dry, dense, fluidized liquid-simulating condition, and as will be hereinafter pointed out, a sufficient amount of catalyst particles is introduced into the reaction zone or vessel (10) to maintain the reaction vessel completely full or flooded with the dense, fluidized mixture.

Dry gaseous reaction products together with catalyst particles pass overhead through line (24) and the mixture is passed to a separating means (26) for separating a large amount of the catalyst particles from the gaseous reaction products. The separating means is shown in the drawing as a cyclone separator but other forms of separating means may be used. The separated catalyst particles are withdrawn from the bottom of the separating means (26) and are introduced into a standpipe (28) which conducts a controlled amount of the separated catalyst particles back into the reaction zone or vessel (10). The intermediate portion of the standpipe (28) is provided with a branch standpipe (29) which opens into the reactor (10) above the distribution plate or grid (14).

The branch standpipe (29) is preferably provided with a control valve or damper (30) in its lower portion to control the flow of catalyst particles from the standpipe (28). With a certain desired concentration of catalyst in reactant gases there is a certain pressure drop through the reactor (10). The concentration may be maintained at about the desired figure by pressure responsive means (31) connected to valve (30) by means (32) for moving valve (30) toward open or closed position as the concentration in reactor (10) varies for any reason.

The density of the fluidized catalyst mixture in the standpipe (28) above branch standpipe (29) is greater than the density of the mixture in the re-

action zone or vessel (10) and by pressure produced by the hydrostatic column, the catalyst is returned from the separating means (26) to the reaction zone or vessel (10). If desired, the standpipe (28) may be provided with one or more fluidizing lines (33) to insure maintaining the particles in fluidized condition in the standpipe.

The rest of the catalyst passes to standpipe (34) which forms a continuation of standpipe (28). The lower portion of standpipe (34) is provided with a control valve (35) responsive to the level of catalyst collecting in cyclone separator (26). A lever control (36) is provided for separator (26) and has means (37) for controlling the position of control valve (35) in standpipe (34) to maintain standpipes (28) and (34) substantially full at all times. From the bottom of standpipe (34) the catalyst passes to regeneration zone (38) as will be hereinafter described in greater detail.

The separated reaction products in gaseous form pass overhead from the separating means (26) through line (39). The reaction products may contain entrained catalyst and it is therefore preferable to pass the reaction products through another separating stage or step to recover an additional quantity of catalyst particles. A quenching medium, such as water, vaporizable liquids generally, or cold catalyst particles, is introduced into line (39) through line (40) to quickly reduce the temperature below the temperature at which side reactions such as polymerization or thermal cracking occur.

The quenched products together with the catalyst particles entrained therein are passed to a second separating means (41) in which the bulk of the catalyst is removed from the gaseous or vaporous products. The separating means is shown in the drawing as a cyclone separator but other forms of separating means may be used. The separated catalyst particles are withdrawn from the bottom of the separating means (41) and passed into a standpipe (42) which returns the separated catalyst particles to the interior of the reaction zone or vessel (10). The bottom of the standpipe (42) may be provided with a control valve (43). The bottom of the standpipe (42) preferably terminates above the distribution plate member (14).

The separated reaction products pass overhead through line (43') and are preferably passed to cyclone separator or the like (44) for separating additional amounts of entrained catalyst. The separated catalyst is returned to reactor

(10) through line (45) which terminates above grid member (14). The separated reaction products pass overhead through line (46) to suitable separation equipment 5 for recovering the desired products.

Instead of returning the separated catalyst particles from the separating means (41) to the reaction zone or vessel (10), the catalyst particles may be withdrawn from 10 the standpipe (42) through a branch line or standpipe (not shown) and passed to the regeneration zone (38) before being returned to the reaction zone (10).

It is necessary to regenerate the catalyst 15 particles before reusing them in another reaction step. One method of regeneration will now be described. Catalyst particles are withdrawn from the lower portion of the dense mixture in the reaction 20 zone (10) through a withdrawal pipe (52) which extends above the distribution plate (14).

The withdrawal pipe (52) forms a standpipe. One or more fluidizing lines (54) 25 may be provided for introducing fluidizing gas into the standpipe (52). The fluidizing gas may also be used to strip vaporizable material from the catalyst particles. The standpipe (52) is provided 30 with a control valve (56) for controlling the rate of withdrawal of the catalyst particles from the reaction zone (10).

Steam is used as the regenerating gas and is introduced through line (58) below 35 valve (35) in standpipe (34) and mixed with the spent or coke-containing catalyst particles from standpipe (34) to make a less dense mixture and this less dense mixture is passed through line (62) for a 40 short distance and is then mixed with spent catalyst from standpipe (52) below valve (56). The total less dense mixture is then passed through line (63) into the bottom portion of the regeneration zone 45 or vessel (38) below a distribution plate or grid member (66) in the bottom portion of the regeneration vessel.

The velocity of the regenerating gas passing upwardly through the regeneration 50 vessel is selected to maintain the catalyst particles in a dense fluidized liquid-simulating condition as shown at (68) having a level indicated at (72). Above the dense phase is a less dense or 55 dilute phase (74) in which the gases contain only a small amount of entrained catalyst particles.

The regeneration gases leave the dense 60 bed or mixture and pass through a separating means (76) arranged in the upper portion of the regeneration vessel (64). Separated catalyst particles are returned to the dense bed or mixture (68) through line (78). Hot regeneration 65 gases leave the separation means (76)

through line (82). The gases passing through line (82) still contain entrained catalyst and it may be desirable to recover this catalyst by passing the gases through additional separating means, 70 such as cyclone separators, a Cottrell precipitator or a scrubbing tower.

Hot regenerated catalyst particles are withdrawn from the lower portion of the dense bed or mixture (68) through withdrawal line or standpipe (84) which 75 extends above the distribution plate (66) and which forms a continuation of the standpipe (16) hereinbefore described.

Fresh make-up catalyst is preferably 80 added to regenerator (38) through line (86).

The butenes to be dehydrogenated admixed with steam are passed through line (12) into the bottom portion of the 85 reaction zone or vessel (10).

For maximum production of butadienes the butene feed comprises butenes-1 and -2 of reasonably high purity. The catalyst should be one not deactivated by 90 steam.

The butene feed is desirably preheated to a temperature of 800° F. to 1000° F., a part of the heat for the process being supplied from the combustion of carbonaceous matter in the regenerator which is preferably at a temperature of 1200— 1500° F. The catalyst comprises any suitable dehydrogenation catalyst, such as oxides of iron, magnesium or copper or 100 mixtures thereof with or without potassium oxide. The catalyst is heated to about a temperature of 1300° F. to 1500° F., preferably about 1400° F.

About 10 to 20 mols. of superheated 105 steam per mol. of feed should be used for regeneration by the water-gas reaction. The temperature during regeneration with steam is about 1200° F. to 1400° F. Heat in addition to that supplied by catalyst in the reaction zone is preferably supplied by superheated steam heated to a temperature above about 1200° F. When using a catalyst containing potassium, it may be desirable to add a potassium compound to replace the potassium 115 lost during the process.

Where regeneration temperatures are much higher than the reaction temperature, the butene feed may be heated to a 120 lower temperature to avoid thermal cracking and when it is mixed with the regenerated catalyst at a higher temperature, the butene feed is raised to the reaction temperature almost instantaneously. Also 125 the steam may be heated to temperatures higher than reaction temperatures before being introduced into the reaction zone to supply heat to the butene feed.

The catalyst is preferably in finely 130

divided or pulverized form of a size between about 50 and 400 standard mesh. However, substantially coarser particles may be used. The butene feed passing upwardly through the reaction zone maintains the catalyst particles in a dry fluidized liquid-simulating condition. When using a catalyst of about 100 to 400 standard mesh, the dense fluidized mixture in the reaction zone or vessel (10) will have a density between about 10 lbs. per cubic foot and 50 lbs. per cubic foot, depending on the rate of addition of catalyst to the reaction zone relative to the vapor rate, and upon the physical characteristics of the catalyst.

The velocity of the butene vapors passing up through the reaction zone may vary between about 3 ft. per second to 50 ft. per second. The reaction time or time of contact of the butene feed with the catalyst particles from the distribution plate (14) to the separating means (26) may vary between about 0.1 seconds to 10 seconds, preferably about 0.1 to 2.0 seconds.

From the above it will be seen that the butene feed passes through the reaction zone at a high velocity, and in order to maintain catalyst within the reaction zone or vessel it is necessary to feed a large amount of catalyst particles to the reaction zone. Part of this catalyst is fed from the standpipe (16) which contains hot regenerated catalyst particles and the rest is supplied by recirculation from the separating means (26) through line (29) and from separating means (41) and (44) through lines (42) and (45), respectively. Due to the high velocity of the vapors and to the feeding of the large amount of catalyst particles to the reaction zone, the reaction zone (10) is completely flooded with catalyst in the dense phase and the gaseous products passing overhead through line (24) are in a dense phase or mixture. The overhead pipe or outlet pipe (24) is really an overflow pipe which permits removal of the dense phase mixture from the top portion of the reaction zone or vessel (10).

Hot regenerated catalyst introduced through standpipe (16) and recirculated catalyst from standpipe (29) and lines (42) and (45) are added to the reactor and the amount of recirculated catalyst added per cubic foot of butene vapor introduced into the reaction zone or vessel (10) approaches half the concentration desired or maintained in the reaction zone at high rates of catalyst addition.

Gaseous reaction products leaving the first separating means (26) through line (39) are quenched by the introduction through line (40) of cool catalyst to a

temperature of about 500° F. to 1000° F., or water may be used as a quenching medium. The reaction products in gaseous form leaving the third separating means (44) through line (46) are passed to any suitable equipment for recovering desired products. The reaction products may be treated with a solvent which is selective for butadiene and the butadiene is then separated from the solvent.

During regeneration, the temperature is maintained between about 1300° F. and 1500° F.

The regenerating steam is heated to a higher temperature than reaction temperature and in addition to steam fuel may be burned in the regeneration zone to supply the heat necessary to raise the temperature of the catalyst particles to above reaction temperature in the reactor.

Instead of withdrawing all the spent catalyst from the bottom of the reaction zone through pipe or standpipe (52), the standpipe (52) may be partially blocked as by a valve and more spent catalyst may be directed to standpipes (28) and (34) and withdrawn therefrom to regenerator (38). When operating in this manner, it may be desirable to introduce part or all of the quench medium from line (40) into line (43) instead of line (39), in order to reduce the amount of quench material required and avoid cooling an excessive quantity of catalyst.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A process for the catalytic dehydrogenation of butenes to produce butadiene comprising introducing a gaseous fluid reactant containing butene, steam and a hydrocarbon dehydrogenation catalyst, not deactivated by steam, in powder form, into the lower portion of a reaction zone, passing the gaseous fluids upwardly through said reaction zone at a velocity sufficient to suspend the catalyst particles in the rising gases and forming a dry dense liquid-like catalyst-gas mixture, maintaining said reaction zone completely full of this fluidized catalyst-gas mixture, removing gaseous fluid reaction products overhead with the catalyst in said catalyst-gas mixture, separating the bulk of the catalyst particles from the removed reaction products, quenching the separated reaction products to a temperature of 500—1000° F. to minimize losses of butadiene, returning a controlled amount of the separated catalyst particles as a confined stream to said reaction zone without regeneration to aid in maintaining the

high concentration of catalyst in said reaction zone, suspending a second portion of said separated catalyst in a stream of steam superheated to a temperature above 1200° F., passing this suspension through a regeneration zone and returning the hot regenerated catalyst to said reaction zone.

2. A process according to Claim 1, wherein the gaseous butene reactant is preheated to 800—1000° F. and the said hot regenerated catalyst is at a temperature of 1200—1500° F.

3. The process according to Claim 1, wherein the hot regenerated catalyst and

recycled catalyst are introduced as dense fluidized mixtures into the dense fluidized mixture in said reaction zone above the place of introduction of the gaseous reactant.

4. Process according to Claim 1, in which the said hydrocarbon dehydrogenation catalyst comprises an oxide of iron.

Dated this 6th day of July, 1945.

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29, Southampton Buildings,
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Agents for the Applicant.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1948.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies, price 1s. 0d. each (inland) 1s. 1d. (abroad) may be obtained.

[This Drawing is a reproduction of the Original on a reduced scale.]

